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Preparation of iPP hollow-fiber microporous membranes via thermally induced phase separation with co-solvents of DBP and DOP

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Abstract

IPP hollow-fiber microporous membranes were prepared via thermally induced phase separation (TIPS) with co-solvent di-n-butyl phthalate (DBP) and dioctyl phthalate (DOP). The DOP mass fraction in co-solvent (α) and iPP mass fraction in a casting solution (β) were worked as the variables in the spinning process. With increasing α, the TIPS of the polymer solution changes to only polymer crystallization from liquid–liquid phase separation with subsequent polymer crystallization. Accordingly, the morphology of the resulting membrane changes from a typical cellular structure to a mixed structure, which is basically cellular but with particulate boundaries, and then a typical particulate structure. As a result, permeability of the membrane increases sharply and mechanical properties of the membrane decrease obviously. Therefore, the iPP hollow-fiber microporous membrane with higher permeability and higher mechanical properties must exhibit a mixed membrane morphology in which liquid–liquid phase separation precedes polymer crystallization. However, by varying β, both the phase separation pattern of the iPP solution and types of the resulting membrane structure cannot be changed. The permeability of resulting membrane decreases with increasing β, but the mechanical properties increase with increasing β. It is noted also that those iPP hollow-fiber microporous membranes are apt to possess a narrow pore size distribution. It is indicated that by choosing proper α and β, the membrane morphology can be an open cellular pore structure; moreover, the resulting membrane exhibits both higher permeability and higher mechanical properties. It is suggested that for a crystalline polymer such as iPP, by a proper approach, adjusting the competition between liquid–liquid phase separation and polymer crystallization is the key to creating the membrane with an interconnecting pore structure and good performance.

Keywords: Thermally induced phase separation; Hollow-fiber membrane; Isotactic polypropylene; Membrane preparation; Morphology; Permeability; Mechanical property

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1. Introduction

Isotactic polypropylene (iPP) is an outstanding membrane material because of its low cost, good mechanical properties, high thermal stability and excellent resistance to acids, alkalis and organic solvents. However, due to the lack of solvent for iPP at room temperature, conventional immersion precipitation to prepare membranes cannot be used. Thermally induced phase separation (TIPS), based on the dependence of polymer solubility on temperature, offers an attractive way to prepare iPP porous membranes where a homogeneous iPP solution is formed by dissolving iPP in diluents at about the melting temperature of pure iPP, and then phase separation is induced by cooling the iPP solution [1].

Numerous studies have reported the effect of diluents on the TIPS of polymer solutions and membrane structures [1–6]. It was revealed that the phase separation mechanism (solid–liquid or liquid–liquid) depends on the interaction parameter (χ) between polymer and diluent. Consequently, the membrane morphology is changed from a spherulitic structure to cellular one with increasing χ [1–4]. Matsuyama et al. [5] reported the effect of three diluents, methyl salicylate (MS), diphenylether (DPE), and diphenylmethane (DPM), on both the phase diagram and droplet growth. The cloud-point curve was shifted to a lower temperature with compatibility increasing in the order of iPP/MS, iPP/DPE, and iPP/DPM. The diluent type did not greatly influence the crystallization temperature. The difference in the droplet sizes in the three systems is attributable to the difference in the time interval for droplet growth. Vadalia et al. [6] prepared microporous membranes by TIPS with a high-density polyethylene (HDPE)/co-solvent of ditrydecyphthalate and hexadecane. Their research indicated that by varying cosolvent composition, the phase diagrams and the membrane morphology could be controlled successfully. These investigations mean that the selection of diluents plays an important role in both the TIPS of polymer solutions and the formation of polymer membranes. However, the effect of diluents on morphology and performances of hollow-fiber membranes has not been widely reported.

Kim et al. [7] prepared iPP hollow-fiber membranes from a polypropylene/soybean oil system by TIPS and subsequent cold stretching. Gu et al. [8] prepared microporous hollow-fiber membranes from blends of isotactic and atactic polypropylene by TIPS and subsequent cold stretching. Sun et al. [9] prepared HDPE hollow-fiber membranes by TIPS of a HDPE/liquid paraffin system. But the pure water fluxes of the membranes mentioned above are quite low. Shang et al. [10] investigated preparation and performance of poly(ethylene-co-vinyl alcohol) (EVOH) hollow-fiber membranes via TIPS of an EVOH/glycerol system. The pure water flux can be improved by increasing the water bath temperature and the take-up speed, and by decreasing ethylene content in EVOH. Both the pore size at the outer surface and the connectivity between the pores has to be considered together to understand the experimental result of the water permeability and the solute rejection. Matsuyama et al. [11] prepared HDPE hollow-fiber membranes by TIPS. Two kinds of diluents, diisodecyl phthalate (DIDP) and liquid paraffin, were used. The use of a polymer with a higher molecular weight, a shorter air gap distance and a higher bath temperature can obtain a higher pure water flux. The liquid–liquid phase separation in the case of DIDP leads to higher permeability than the polymer crystallization in the case of liquid paraffin. However, the literature [10,11] did not report the effect of diluents on mechanical properties of the resulting hollow-fiber membranes. It is unknown whether the resulting membranes could be used for industrial applications.

In our previous work [12], the TIPS thermodynamics of the ternary solution consisting of iPP, di-n-butyl phthalate (DBP, a poor solvent)